First Hit Previous Doc Next Doc Go to Doc#

Generate Collection | Print

L1: Entry 4 of 4 File: DWPI Nov 4, 1994

DERWENT-ACC-NO: 1995-025666
DERWENT-WEEK: 199504

TITLE: Mfg. oxide superconductivity wire - involves heating metal pipe filled with powder of oxide superconductive body and sintering to form sintered body of oxide superconductive body

PRIORITY-DATA: 1993JP-0119043 (April 21, 1993)

Search Selected | Search ALL | Clear

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 06309967 A	November 4, 1994		004	H01B013/00

INT-CL (IPC): B21F 19/00; H01B 12/04; H01B 13/00

ABSTRACTED-PUB-NO: JP 06309967A
BASIC-ABSTRACT:

The manufacturing method of an oxide superconductivity wire involves filling of a metal pipe (1) with powder of an oxide superconductive body at a temperature of 200-800 deg.C. Then it is processed so that the powder is made into a shape of wire. Next sintering processing is carried out in a vacuum enclosure which results in the formation of a sintered body of an oxide superconductive body (2).

ADVANTAGE - Provides good superconductivity. Provides homogeneity of cross sectional shape. Improves manufacturing efficiency of oxide superconductivity wire. Avoids problem of swelling.

Previous Doc Next Doc Go to Doc#

First Hit Previous Doc Next Doc Go to Doc#

Generate Collection Print

L1: Entry 2 of 4 File: JPAB Nov 4, 1994

PUB-NO: JP406309967A
DOCUMENT-IDENTIFIER: JP 06309967 A
TITLE: MANUFACTURE OF OXIDE TYPE SUPERCONDUCTING WIRE

PUBN-DATE: November 4, 1994

INVENTOR-INFORMATION:

NAME	COUNTRY
SUKETANI, SHIGENORI	
HIRAOKA, MAKOTO	

INT-CL (IPC): H01B 13/00; B21F 19/00; H01B 12/04

ABSTRACT:

PURPOSE: To provide an oxide type superconducting wire of metal cover type which can perform sintering process without swelling, etc., even in the case of a long stretching body and excels in the evenness in the section shape and in the superconductive characteristics.

CONSTITUTION: A rod-form shaping consisting of powder of oxide superconductor is vacuum encapsulated in a metal pipe 1 in the condition decompressed below 1/103Torr under a heating to 200-800°C, and the resultant is, if necessary, subjected to a diametric contraction and processed into a wire form, followed by a sintering process, and a sintered body 2 is obtained in which the internal oxide superconductor is consolidated. This allows producing an oxide superconducting wire which excels in the filling effectiveness into the metal pipe according to the shaping body system and which is manufacturable effectively and stably.

Previous Doc Next Doc Go to Doc#

CLAIMS

[Claim(s)]
[Claim 1] The manufacture method of the oxide superconductivity line characterized by processing a wire rod form after carrying out vacuum enclosure of the rod-like forming object which consists of powder of an oxide superconductivity object into a metal pipe in the state where it decompressed under 200-800-degree C heating at 1/103 or less Torr, carrying out sintering processing of it, and making an internal oxide superconductivity object unify.
[Claim 2] The manufacture method according to claim 1 with which processing to a wire rod form is presented after carrying out diameter reduction processing of the vacuum enclosure thing.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manufacture method of a metallic coating type oxide superconductivity line of having prevented sintering ****.
[0002]
[Description of the Prior Art] Conventionally, filled up the metal pipe with the powder of the oxide superconductivity object, and heat-treated, the powder of the oxide superconductivity object was made to sinter after processing wire rod forms, such as a wire and a tape, and the manufacture method of the superconducting wire of having a sintered compact 2 inside the metallic coating layer 1 like illustration at drawing 5 was known. However, there was a problem that swelled at the time of sintering, produced 11 (expansion part) etc., and a uniform-shaped superconducting wire was not formed. this -- swelling -- etc. -- generating also had the problem that the **** induced the crack in a sintered compact (superconductivity layer), and reduced the superconductivity characteristics, such as critical current density, while it was remarkable and

became an obstacle at the time of processing it into a coil etc., especially when the long body of several 10cm or more was acquired.

[0003]

[Problem to be solved by the invention] also in the case of the long body, this invention swells -- etc. -- sintering processing can be carried out without generating and let development of the manufacture method of a metallic coating type oxide superconductivity line of excelling in homogeneity-shaped [cross-sectional] or the superconductivity characteristic be a technical problem.

[0004]

[Means for solving problem] This invention the rod-like forming object which consists of powder of an oxide superconductivity object in a metal pipe Under 200-800-degree C heating, After carrying out vacuum enclosure in the state where it decompressed to 1/103 or less Torr and carrying out diameter reduction processing if needed, a wire rod form is processed, and the manufacture method of the oxide superconductivity line characterized by carrying out sintering processing of it and making an internal oxide superconductivity object unify is offered.

[0005]

[Function] swelling by the above-mentioned method of carrying out heating vacuum enclosure of the forming object which consists of powder of an oxide superconductivity object into a metal pipe, and performing predetermined processing also in the case of the long body -- etc. -- sintering processing can be carried out without generating and the metallic coating type oxide superconductivity line which is excellent in the homogeneity of cross-sectional form or the superconductivity characteristic is obtained.

[0006] Although it is thought that sintering **** is produced from the above when the carbon which the powder of an oxide superconductivity object contains, the carbon dioxide by which this powder was adsorbed, moisture, the gas further mixed at the time of restoration, etc. gasify or expand at the time of sintering processing A gasification ingredient etc. is removed, in order to use the powder concerned as a rod-like forming object in this invention and to carry out heating vacuum enclosure of it into a metal pipe moreover. Since each powder is enclosed in a metal pipe with the efficient restoration workability in the state where the gasification ingredient and mixing gas at the time of sintering processing are hardly included, it is thought that sintering **** is prevented.

[0007]

[Working example] The manufacture method of this invention is a thing which carried out heating vacuum enclosure of the rod-like forming object which consists of powder of an oxide superconductivity object into the metal pipe, and processed the wire rod form and which carries out back sintering processing, is made to unify an internal oxide superconductivity object, and obtains a metallic coating type oxide superconductivity line. The oxide

superconductivity line concerning drawing 1 , drawing 2 , and drawing 3 was illustrated. It is the sintered compact which the metallic coating layer (metal pipe) unified in 1, and the oxide superconductivity object unified in 2.

[0008] The rod-like forming object which consists of powder of an oxide superconductivity object can be acquired to drawing 4 , for example by a powder-compacting fabrication method with a proper hydrostatic pressure pressurization fabrication method between the colds like illustration etc. In addition, in drawing 4 , the form block which 3 becomes from rubber etc., and 21 are rod-like forming objects which consist of powder of an oxide superconductivity object. A rod-like forming object can be made into a proper form according to the cross-sectional form of the oxide superconductivity line made into the purpose etc.

[0009] There is no limitation in particular about the kind of oxide superconductivity object which forms the powder with which fabrication is presented. As the example, Bi system oxide superconductivity object like Bi2Sr2CaCu2Oy or Bi2-xPbxSr2Ca2Cu3Oy, Y system oxide superconductivity object like YBa2Cu3Oy or YBa2Cu4Oy, Ba system oxide superconductivity object like Ba1-xKxBiO3, Nd system oxide superconductivity object like Nd2-xCexCuOy, other La system oxide superconductivity objects, Tl system oxide superconductivity object, Pb system oxide superconductivity object, etc. are raised.

[0010] Moreover, the thing which replaced ingredients, such as what replaced ingredients, such as above Bi, by other rare earth elements, and Sr, with other alkaline-earth metals, or the thing which replaced O ingredient by F etc. is raised. Furthermore, the thing which made the pinning center contain is raised. The oxide superconductivity object of pinning center content has the advantage which shows big critical current density under a high magnetic field according to the pin stop effect of the magnetic flux by the pinning center. The oxide superconductivity object of pinning center content can be acquired, for example by the MPMG method (Melt Powdering Melt Growth) etc.

[0011] 0.1-10 micrometers of 100 micrometers or less are suitable for the particle diameter of the powder used for fabrication above all. The powder can be obtained by grinding the temporary-quenching object or sintered compact of an oxide superconductivity object, for example. As for the powder to be used, what repeated temporary quenching, pulverization processing, etc. and removed the gasification ingredient at the time of sintering as much as possible is desirable.

[0012] Temporary quenching for removing the aforementioned gasification ingredient, for example In the case of the powder of a Bi2Sr2CaCu2Oy system oxide superconductivity object Since the weight reduction also with the high temperature side of 800 degrees C of abbreviation for the second time is shown after [600 / about] weight reduction is first shown by the about 70 - low temperature side of 500 degrees C of abbreviation -, it is desirable to process with the highest temperature in which weight reduction appears based on the weight

reduction curve according to sintering conditions etc.

[0013] In addition, in the above, weight reduction at low temperature is considered that the weight reduction in high temperature is based on the ingredient combined with large binding energies, such as hydration, based on evaporation for absorptive water. Therefore, as for temporary quenching treatment, generally, it is desirable to carry out at sintering temperature or a temperature a little lower than it. Moreover, as for temporary quenching treatment, it is desirable to carry out under oxygen gas atmosphere. In the temporary quenching treatment under air atmosphere, a gasification ingredient may fully be unable to be removed.

[0014] Moreover, you may present restoration enclosure into a metal pipe in the state where carried out temporary quenching treatment of the rod-like forming object which consists of powder of an oxide superconductivity object, and it was considered as the temporary-quenching object from the point of removing the gasification ingredient at the time of sintering as much as possible in this invention. Therefore, the aforementioned temporary-quenching object is also included in the rod-like forming object which consists of powder of the oxide superconductivity object in this invention. In addition, an opportunity to adsorb the gasification ingredient at the time of sintering processing is reduced, while it is also controlled by temporary-quenching embodying of a rod-like forming object that gas mixes at the time of the restoration to a metal pipe, the causative agent of sintering **** is removed from a forming object by it at the time of temporary quenching, and re-adsorption is also controlled.

[0015] As a metal pipe for carrying out vacuum enclosure of the rod-like forming object which consists of powder of an oxide superconductivity object, the thing of a proper cross-sectional form which can accommodate a rod-like forming object can be used, and it can also be considered as division forms, such as half-segmented. As a metal kind which forms a metal pipe, what is excellent in oxidation resistance or processability is desirable. the alloy which contains silver, gold, platinum, and this metal as the example -- the high-melting point alloy like silver and a platinum alloy, and silver and a palladium alloy etc. is raised above all.

[0016] In the above, the metal pipe may be formed by the composite material which carried out distributed content of alumina, chromic oxide, silica, zirconia, Chita Near, a flower of zinc, a calcium oxide, manganese oxide, iron oxide, cobalt oxide, and the oxide particulates like vanadium oxide, for example. This composite-izing may be effective in the improvement of mechanical properties, such as intensity, and the improvement in the superconductivity characteristic at the time of processing a metal pipe as an enveloping layer of a powder layer or a superconductivity layer.

[0017] Vacuum enclosure of the 1/103 or less Torr of the rod-like forming object which consists of powder of an oxide superconductivity object in this invention is preferably carried out into a metal pipe under 200-800-degree C heating in the state where it decompressed to 1/105 or less Torr. The method which carries out vacuum suction of the inside of a pipe, and seals the

opening end of a pipe while this vacuum enclosure heats the rod-like forming object concerned to predetermined temperature after filling up a metal pipe, for example, After placing the metal pipe which filled up with the rod-like forming object concerned the decompression atmosphere adjusted to a predetermined temperature and a predetermined degree of vacuum and considering it as vacuum enclosure conditions, a method with a proper method which seals the opening end of a pipe may perform. The seal processing can take proper closure means, such as sticking by pressure, and press processing, sealing.

[0018] After processing it into the target wire rod form, sintering processing is presented, but the metal pipe which enclosed the rod-like forming object may give diameter reduction processing, before processing a wire rod form if needed in this invention. This diameter reduction processing is effective in the improvement in the processability to a wire rod form, as a result improvement in the superconductivity characteristic for the purpose of losing the opening between a rod-like forming object and a rod-like metal pipe. In addition, a method with a dice method, proper sizing method or forge method, etc. may perform diameter reduction processing.

[0019] Proper methods, such as small-gage-wire-izing by the **** processing which minded the dice etc., for example, and shape[of a tape]-izing by the rolling processing through a pinch roll etc., may perform processing to the predetermined wire rod form of the metal pipe which enclosed the rod-like forming object. A metal pipe is changed into the metallic coating layer to an internal oxide superconductivity object by processing to this wire rod form.

[0020] In addition, in this invention, you may perform press processing the time of processing to a wire rod form, and after the processing (before sintering processing). Press processing is effective in stabilization of quality, or improvement. Moreover, press processing may be repeated two or more times, and a heating process is established among press processings in front and behind in that case.

[0021] Sintering processing is for bulk-izing the oxide superconductivity object in a metallic coating layer, and making it unify. In this invention, you may perform sintering processing to what was made into secondary forms, such as a coil. Sintering temperature is suitably determined according to the kind of oxide superconductivity object. Generally it is 700-1200 degrees C. Moreover, you may perform sintering processing under pressurization atmosphere by accommodating a sintering subject in the heat-resistant resisting pressure container of a sealing system. Pressurization atmosphere acts as the external pressure which prevents generating of sintering ****.

[0022] For example according to kinds of oxide superconductivity object, such as oxygen gas atmosphere, air atmosphere, and nitrogen-gas-atmosphere mind (content of oxygen gas is possible), you may determine a sintering atmosphere suitably. Although the sintering processing in dryness atmosphere can prevent moisture participation and is desirable, not

necessarily considering it as dryness atmosphere in this invention does not require it. Moreover, on the occasion of sintering processing, a closure state is still sufficient as the end of a metallic coating layer (metal pipe), and it is good also as an opening state.

[0023] [the powder of 0.1-10 micrometers of particle diameter of a Bi1.8Pb0.4Sr2Ca2Cu3Oy system oxide superconductivity object which obtained the operation which carries out temporary quenching at 830 degrees C among the example 1 atmosphere for 20 hours, and grinds it by having repeated it 3 times] It fabricated by the hydrostatic pressure pressurization method between the colds depended on a rubber type, and the rod-like forming object 6.0mm in diameter and 100mm in length was acquired.

[0024] Next, a silver pipe with a thickness of 1.0mm and an inside diameter of 7.0mm is filled up with the aforementioned rod-like forming object. After carrying out vacuum suction from the other end after welding and closing that one end until the decompression state of 1/106 or less Torr is stably shown under about 500-degree C heating atmosphere, this opening end is stuck by pressure. Subsequently, after welding and closing and carrying out **** processing of it through a dice at 3mm of outer diameters, It rolled with a pinch roll, and was processed into the tape 3mm in width, 0.3mm (100 micrometers in thickness of a superconductivity part) in thickness, and about 10m in length, press processing was performed to it after about 150-hour heating at 830 degrees C, it heated at 830 degrees C for about 50 hours, sintering processing was carried out in the atmosphere, and the oxide superconductivity line was obtained. Sintering **** was not accepted in the obtained oxide superconductivity line. Moreover, the critical temperature was 108K and critical current density was 22000 A/cm2 (77K).

[0025] Before example 2 **** processing, diameter reduction processing of the vacuum enclosure thing was carried out by the forge method at about 6.5mm of outer diameters, and also the oxide superconductivity line was obtained according to the example 1. Sintering **** was not accepted in the obtained oxide superconductivity line. Moreover, the critical temperature was 106 and critical current density was 19000 A/cm2 (77K).

[0026] Only filled up the silver pipe, tape-ized, and sintering processing was carried out in the state of the both-ends opening, without carrying out heating vacuum processing of the comparative example 1 cylindrical fabrication object, and also the oxide superconductivity line about 10m in length was obtained according to the example 1. However, sintering **** was accepted in the obtained oxide superconductivity line in many parts. Moreover, the critical temperature was 105K and critical current density was 5000 A/cm2 (77K).

[0027] The metal pipe was filled up as it is, without processing the powder of a comparative example 2 oxide-superconductivity object into a rod-like forming object, and also the oxide superconductivity line about 10m in length was obtained according to the comparative example 1. However, sintering **** was accepted in the obtained oxide superconductivity line in many parts. Moreover, the critical temperature was 105K and critical current density was 4000 A/cm2

(77K).

[0028] In addition, in the above, the critical temperature is temperature when the temperature change of electrical resistance is measured by 4 terminal method under the current density of 10 A/cm2, cooling with a freezer and the generating voltage between voltage terminals is set to 0.

[0029] Moreover, critical current density is the value which **(ed) the current value when cool to 77K in liquid nitrogen with a power lead, a current value is raised gradually, change by the impression current of the voltage between voltage terminals is measured by 4 terminal method and the voltage of 1microv/cm appears in a X-Y recorder with the cross-section area of the superconductivity object.

[0030]

[Effect of the Invention] According to this invention, the long body of a metallic coating type oxide superconductivity line without sintering **** can be acquired by being stabilized in the state of excelling in homogeneity-shaped [cross-sectional] and the superconductivity characteristic. Moreover, it excels in the restoration workability to the metal pipe by a forming object method, and excels in the manufacture efficiency of the oxide superconductivity line.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The sectional view which illustrated the oxide superconductivity line.

[Drawing 2] The sectional view which illustrated other oxide superconductivity lines.

[Drawing 3] Furthermore, the sectional view which illustrated other oxide superconductivity lines.

[Drawing 4] The cross-sectional explanatory view of the example of a manufacturing process.

[Drawing 5] The partial section perspective view of the conventional example.

[Explanations of letters or numerals]

1: Metallic coating layer

2: The sintered compact of an oxide superconductivity object

21: A rod-like forming object

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)**公開特許公報（Ａ）**　(11)特許出願公開番号

特開平6－309967

(43)公開日　平成６年(1994)11月４日

(51)Int.Cl.[5]	識別記号	庁内整理番号	Ｆ Ｉ	技術表示箇所
Ｈ０１Ｂ　13/00	５６５　Ｄ	7244－5G		
Ｂ２１Ｆ　19/00	ＺＡＡ　Ｇ	9264－4E		
Ｈ０１Ｂ　12/04	ＺＡＡ	7244－5G		

審査請求　未請求　請求項の数２　ＦＤ　（全　４　頁）

(21)出願番号　特願平5－119043

(22)出願日　平成５年(1993)４月21日

(71)出願人　000003263
三菱電線工業株式会社
兵庫県尼崎市東向島西之町８番地

(72)発明者　佑谷　重徳
兵庫県尼崎市東向島西之町８番地　三菱電線工業株式会社内

(72)発明者　平岡　誠
兵庫県尼崎市東向島西之町８番地　三菱電線工業株式会社内

(74)代理人　弁理士　藤本　勉

(54)【発明の名称】　酸化物超電導線の製造方法

(57)【要約】

【目的】　長尺体の場合にも脚れ等の発生なく焼結処理でき、断面形状の均一性や超電導特性に優れる金属被覆型の酸化物超電導線を得ること。

【構成】　酸化物超電導体の粉末からなる棒状成形体を金属パイプ（１）内に２００～８００℃の加熱下、１／１０^{3}Ｔｏｒｒ以下に減圧した状態で真空封入し、必要に応じて縮径加工したのち線材形態に加工し、それを焼結処理して内部の酸化物超電導体を一体化（２）させる酸化物超電導線の製造方法。

【効果】　成形体方式による金属パイプへの充填作業性に優れて酸化物超電導線が製造効率よく安定に得られる。

1

【特許請求の範囲】

【請求項１】　酸化物超電導体の粉末からなる棒状成形体を金属パイプ内に２００～８００℃の加熱下、１／１０^{3}Ｔｏｒｒ以下に減圧した状態で真空封入したのち線材形態に加工し、それを焼結処理して内部の酸化物超電導体を一体化させることを特徴とする酸化物超電導線の製造方法。

【請求項２】　真空封入物を縮径加工したのち線材形態への加工に供する請求項１に記載の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、焼結膨れを防止した金属被覆型の酸化物超電導線の製造方法に関する。

【０００２】

【従来の技術】従来、酸化物超電導体の粉末を金属パイプに充填して丸線やテープ等の線材形態に加工後、加熱処理して酸化物超電導体の粉末を焼結させ、図５に例示の如き金属被覆層１の内部に焼結体２を有する超電導線の製造方法が知られていた。しかしながら、焼結時に膨れ１１（膨張部）等を生じて均一形状の超電導線が形成されない問題点があった。かかる膨れ等の発生は、数１０cm以上の長尺体を得る場合に特に顕著でコイル等に加工する際の障害になると共に、その膨れが焼結体（超電導層）でのクラックを誘起して臨界電流密度等の超電導特性を低下させる問題点もあった。

【０００３】

【発明が解決しようとする課題】本発明は、長尺体の場合にも膨れ等の発生なく焼結処理できて、断面形状の均一性や超電導特性に優れる金属被覆型の酸化物超電導線の製造方法の開発を課題とする。

【０００４】

【課題を解決するための手段】本発明は、酸化物超電導体の粉末からなる棒状成形体を金属パイプ内に２００～８００℃の加熱下、１／１０^{3}Ｔｏｒｒ以下に減圧した状態で真空封入し、必要に応じて縮径加工したのち線材形態に加工し、それを焼結処理して内部の酸化物超電導体を一体化させることを特徴とする酸化物超電導線の製造方法を提供するものである。

【０００５】

【作用】酸化物超電導体の粉末からなる成形体を金属パイプ内に加熱真空封入して所定の処理を施す上記の方法により、長尺体の場合にも膨れ等の発生なく焼結処理でき、断面形状の均一性や超電導特性に優れる金属被覆型の酸化物超電導線が得られる。

【０００６】前記より、焼結膨れは酸化物超電導体の粉末が含有する炭素や、かかる粉末に吸着された炭酸ガスや水分、さらには充填時に混入した気体等が焼結処理時にガス化ないし膨張することにより生じるものと考えられるが、本発明では当該粉末を棒状成形体とし、しかもそれを金属パイプ内に加熱真空封入するためガス化成分

2

等が除去されて、その効率的な充填作業性と共に個々の粉末が焼結処理時のガス化成分や混入気体を殆ど含まない状態で金属パイプ内に封入されることから焼結膨れが防止されるものと考えられる。

【０００７】

【実施例】本発明の製造方法は、酸化物超電導体の粉末からなる棒状成形体を金属パイプ内に加熱真空封入して線材形態に加工したのち焼結処理し内部の酸化物超電導体を一体化させて、金属被覆型の酸化物超電導線を得るものである。図１、図２、図３にかかる酸化物超電導線を例示した。１が金属被覆層（金属パイプ）、２が酸化物超電導体が一体化した焼結体である。

【０００８】酸化物超電導体の粉末からなる棒状成形体は、例えば図４に例示の如き冷間静水圧加圧成形方式などの適宜な圧粉成形方式で得ることができる。なお図４において、３はゴム等からなる成形型、２１は酸化物超電導体の粉末からなる棒状成形体である。棒状成形体は、目的とする酸化物超電導線の断面形態等に応じて適宜な形態とすることができる。

【０００９】成形に供する粉末を形成する酸化物超電導体の種類については特に限定はない。その例としては、$Bi_2Sr_2CaCu_2O_y$や$Bi_{2-x}Pb_xSr_2Ca_2Cu_3O_y$の如きＢｉ系酸化物超電導体、$YBa_2Cu_3O_y$や$YBa_2Cu_4O_y$の如きＹ系酸化物超電導体、$Ba_{1-x}K_xBiO_3$の如きＢａ系酸化物超電導体、$Nd_{2-x}Ce_xCuO_y$の如きＮｄ系酸化物超電導体、その他Ｌａ系酸化物超電導体、Ｔｌ系酸化物超電導体、Ｐｂ系酸化物超電導体などがあげられる。

【００１０】また、前記のＢｉ等の成分を他の希土類元素で置換したもの、Ｓｒ等の成分を他のアルカリ土類金属で置換したもの、あるいはＯ成分をＦなどで置換したものなどもあげられる。さらに、ピンニングセンターを含有させたものなどもあげられる。ピンニングセンター含有の酸化物超電導体は、そのピンニングセンターによる磁束のピン止め効果により、高い磁場下においても大きな臨界電流密度を示す利点を有する。ピンニングセンター含有の酸化物超電導体は、例えばＭＰＭＧ法（Melt Powdering Melt Growth）などにより得ることができる。

【００１１】成形に用いる粉末の粒径は、１００μm以下、就中０．１～１０μmが適当である。その粉末は、例えば酸化物超電導体の仮焼体ないし焼結体を粉砕することにより得ることができる。用いる粉末は、仮焼・粉砕処理等を繰り返すなどして焼結時のガス化成分を可及的に除去したものが好ましい。

【００１２】前記のガス化成分を除去するための仮焼は、例えば$Bi_2Sr_2CaCu_2O_y$系酸化物超電導体の粉末の場合、約７０～約５００℃の低温側で先ず重量減少を示したのち約６００～約８００℃の高温側でも再度の重量減少を示すことから、焼結条件等に応じた重量減少曲線などに基づき重量減少が現れる最高温度で処理するこ

とが望ましい。

【0013】なお前記において、低温での重量減少は吸着水分の蒸発に基づき、高温での重量減少は水和等の大きい結合エネルギーで結合した成分に基づくと思われる。従って仮焼処理は、焼結温度ないしそれよりも若干低い温度で行うことが一般的に好ましい。また仮焼処理は、酸素ガス雰囲気下で行うことが好ましい。空気雰囲気下での仮焼処理では、ガス化成分の除去を充分に行えない場合がある。

【0014】また本発明においては焼結時のガス化成分を可及的に除去する点より、酸化物超電導体の粉末からなる棒状成形体を仮焼処理し、仮焼体とした状態で金属パイプ内への充填封入に供してもよい。従って本発明における酸化物超電導体の粉末からなる棒状成形体には、前記の仮焼体も含まれる。なお棒状成形体の仮焼体化により、焼結処理時のガス化成分を吸着する機会が低減され、金属パイプへの充填時に気体が混入することも抑制されると共に、焼結脚れの原因物質が仮焼時に成形体より除去されて再吸着も抑制される。

【0015】酸化物超電導体の粉末からなる棒状成形体を真空封入するための金属パイプとしては、棒状成形体を収容できる適宜な断面形態のものを用いることができ、半割等の分割形態とすることもできる。金属パイプを形成する金属種としては、耐酸化性や加工性に優れるものが好ましい。その例としては、銀、金、白金、かかる金属を含有する合金、就中、銀・白金合金、銀・パラジウム合金の如き高融点合金などがあげられる。

【0016】前記において金属パイプは、例えばアルミナ、酸化クロム、シリカ、ジルコニア、チタニア、亜鉛華、酸化カルシウム、酸化マンガン、酸化鉄、酸化コバルト、酸化バナジウムの如き酸化物微粒子を分散含有させた複合材料で形成されていてもよい。かかる複合化は、金属パイプを粉末層ないし超電導層の被覆層として加工した場合における強度等の機械的特性の改良や超電導特性の向上に有効な場合がある。

【0017】本発明において酸化物超電導体の粉末からなる棒状成形体は、200～800℃の加熱下、$1/10^3$Torr以下、好ましくは$1/10^5$Torr以下に減圧した状態で金属パイプ内に真空封入される。かかる真空封入は、例えば当該棒状成形体を金属パイプに充填後、所定温度に加熱すると共にパイプ内を真空引きしてパイプの開口端を密封する方式や、所定の温度と真空度に調節した減圧雰囲気に当該棒状成形体を充填した金属パイプを置いて真空封入条件としたのちパイプの開口端を密封する方式などの適宜な方式で行ってよい。密封処理は、圧着やプレス処理、密栓等の適宜な封止手段を採ることができる。

【0018】棒状成形体を封入した金属パイプは、それを目的の線材形態に加工したのち焼結処理に供されるが、本発明においては必要に応じて線材形態に加工する前に縮径加工を施してもよい。この縮径加工は、棒状成形体と金属パイプとの間の空隙をなくすことを目的とし、線材形態への加工性の向上、ひいては超電導特性の向上に有効である。なお縮径加工は、ダイス方式やサイジング方式、あるいは鍛造方式などの適宜な方式で行ってよい。

【0019】棒状成形体を封入した金属パイプの所定の線材形態への加工は、例えばダイス等を介した伸線処理による細線化や、ピンチロール等を介した圧延処理によるテープ状化などの適宜な方式で行ってよい。この線材形態への加工により金属パイプが、内部の酸化物超電導体に対する金属被覆層へと変形させられる。

【0020】なお本発明においては、線材形態への加工時やその加工後（焼結処理前）にプレス処理を施してもよい。プレス処理は、品質の安定化、ないし向上に有効である。また、プレス処理は複数回繰り返してもよく、その場合には前後のプレス処理間に加熱工程が設けられる。

【0021】焼結処理は、金属被覆層中の酸化物超電導体をバルク化して一体化させるためのものである。本発明では、コイル等の二次形態としたものに対して焼結処理を施してもよい。焼結温度は、酸化物超電導体の種類に応じて適宜に決定される。一般には700～1200℃である。また焼結処理は、密閉系の耐熱耐圧容器に焼結対象物を収容するなどして加圧雰囲気下に行ってもよい。加圧雰囲気は、焼結脚れの発生を防止する外圧として作用する。

【0022】焼結雰囲気は、例えば酸素ガス雰囲気、空気雰囲気、窒素ガス雰囲気（酸素ガスの含有可）などの、酸化物超電導体の種類に応じて適宜に決定してよい。乾燥雰囲気での焼結処理は、水分関与を防止できて好ましいが、本発明においては必ずしも乾燥雰囲気とすることは要しない。また焼結処理に際し金属被覆層（金属パイプ）の端部は、封止状態のままでもよいし、開口状態としてもよい。

【0023】実施例1

大気中、830℃で20時間仮焼し、それを粉砕する操作を3回繰り返して得た$Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_3O_y$系酸化物超電導体の粒径0.1～10μmの粉末を、ゴム型による冷間静水圧加圧方式で成形し、直径6.0mm、長さ100mmの棒状成形体を得た。

【0024】次に前記の棒状成形体を肉厚1.0mm、内径7.0mmの銀パイプに充填し、その一端を溶接して封止した後、約500℃の加熱雰囲気下で$1/10^6$Torr以下の減圧状態を安定に示すまで他端より真空引きしたのちこの開口端を圧着し、次いで溶接して封止しそれをダイスを介し外径3mmに伸線処理した後、ピンチロールで圧延して幅3mm、厚さ0.3mm（超電導部の厚さ100μm）、長さ約10mのテープに加工し830℃で約150時間加熱後、それにプレス処理を施して83

5

0℃で約５０時間加熱して大気中で焼結処理し、酸化物超電導線を得た。得られた酸化物超電導線に焼結脹れは認められなかった。また、その臨界温度は１０８Ｋであり、臨界電流密度は２２０００Ａ／cm²（７７Ｋ）であった。

【００２５】実施例２

伸線処理前に、真空封入物を鍛造方式で外径約６．５mmに縮径加工したほかは実施例１に準じて酸化物超電導線を得た。得られた酸化物超電導線に焼結脹れは認められなかった。また、その臨界温度は１０６であり、臨界電流密度は１９０００Ａ／cm²（７７Ｋ）であった。

【００２６】比較例１

棒状成形体を加熱真空処理することなく単に銀パイプに充填してテープ化し、両端開口状態で焼結処理したほかは実施例１に準じて長さ約１０mの酸化物超電導線を得た。しかし、得られた酸化物超電導線には焼結脹れが多数の個所に認められた。また、その臨界温度は１０５Ｋであり、臨界電流密度は５０００Ａ／cm²（７７Ｋ）であった。

【００２７】比較例２

酸化物超電導体の粉末を棒状成形体に加工することなくそのまま金属パイプに充填したほかは比較例１に準じて長さ約１０mの酸化物超電導線を得た。しかし、得られた酸化物超電導線には焼結脹れが多数の個所に認められた。また、その臨界温度は１０５Ｋであり、臨界電流密度は４０００Ａ／cm²（７７Ｋ）であった。

6

【００２８】なお前記において、臨界温度は１０Ａ／cm²の電流密度下、冷凍機で冷却しながら４端子法で電気抵抗の温度変化を測定し、電圧端子間の発生電圧が０となったときの温度である。

【００２９】また臨界電流密度は、パワーリードと共に液体窒素中で７７Ｋに冷却し、徐々に電流値を上げて、４端子法により電圧端子間の電圧の印加電流による変化を測定し、Ｘ－Ｙレコーダにおいて１μv／cmの電圧が出現したときの電流値を超電導体の断面積で除した値である。

【００３０】

【発明の効果】本発明によれば、焼結脹れのない金属被覆型の酸化物超電導線の長尺体を、断面形状の均一性及び超電導特性に優れる状態で安定して得ることができる。また成形体方式による金属パイプへの充填作業性に優れて酸化物超電導線の製造効率に優れている。

【図面の簡単な説明】

【図１】酸化物超電導線を例示した断面図。

【図２】他の酸化物超電導線を例示した断面図。

【図３】さらに他の酸化物超電導線を例示した断面図。

【図４】製造工程例の断面説明図。

【図５】従来例の部分断面斜視図。

【符号の説明】

１：金属被覆層

２：酸化物超電導体の焼結体

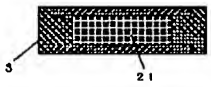
２１：棒状成形体

【図１】

【図２】

【図３】

【図４】



【図５】